

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
REQUEST FOR FILING NATIONAL PHASE OF
PCT APPLICATION UNDER 35 U.S.C. 371 AND 37 CFR 1.494 OR 1.495**

To: Asst. Commissioner of Patents
and Trademarks
Washington, D.C. 20231

(Our Deposit Account No. 03-3975)

09/647479

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)

Atty Dkt: PM 271586 /SMC60285/UST
M# /Client Ref.

From: Pillsbury Madison & Sutro LLP, IP Group:

Date: September 29, 2000

This is a **REQUEST** for **FILING** a PCT/USA National Phase Application based on:

1. International Application <u>PCT/GB99/00655</u> <u>↑ country code</u>	2. International Filing Date 05 MAR 1999 Day MONTH Year	3. Earliest Priority Date Claimed 31 MAR 1998 Day MONTH Year (use item 2 if no earlier priority)
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4. Measured from the earliest priority date in item 3, this PCT/USA National Phase Application Request is being filed within:

(a) ☐ 20 months from above item 3 date (b) ☒ 30 months from above item 3 date,

(c) Therefore, the due date (unextendable) is September 30, 2000

5. Title of Invention COMPOSITION BASED ON WATER-DISSIPATABLE POLYURETHANE

6. Inventor(s) MEYRICK, Barry et al

Applicant herewith submits the following under 35 U.S.C. 371 to effect filing:

7. ☒ Please immediately start national examination procedures (35 U.S.C. 371 (f)).

8. ☒ **A copy of the International Application** as filed (35 U.S.C. 371(c)(2)) is transmitted herewith (file if in English but, if in foreign language, file only if not transmitted to PTO by the International Bureau) including:

a. ☒ Request;

b. ☒ Abstract;

c. 19 pgs. Spec. and Claims;

d. sheet(s) Drawing which are ☐ informal ☐ formal of size ☐ A4 ☐ 11"

9. ☒ **A copy of the International Application has been transmitted by the International Bureau.**

10. **A translation of the International Application** into English (35 U.S.C. 371(c)(2))

a. ☐ is transmitted herewith including: (1) ☐ Request; (2) ☐ Abstract;

(3) pgs. Spec. and Claims;

(4) sheet(s) Drawing which are:

☐ informal ☐ formal of size ☐ A4 ☐ 11"

b. ☐ is not required, as the application was filed in English.

c. ☐ is not herewith, but will be filed when required by the forthcoming PTO Missing Requirements Notice per Rule 494(c) if box 4(a) is X'd or Rule 495(c) if box 4(b) is X'd.

d. ☐ Translation verification attached (not required now).

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500 Rec'd PCT/PTO 29 SEP 2000

11. ☒ **PLEASE AMEND** the specification before its first line by inserting as a separate paragraph:
- a. ☒ --This application is the national phase of international application PCT/GB99/00655 filed March 5, 1999 which designated the U.S.--
- b. ☐ --This application also claims the benefit of U.S. Provisional Application No. 60/_____, filed _____--
12. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)), i.e., **before 18th month from first priority date above in item 3, are transmitted herewith (file only if in English) including:**
13. ☒ PCT Article 19 claim amendments (if any) have been transmitted by the International Bureau
14. ☐ Translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)), i.e., of **claim amendments** made before 18th month, **is attached (required by 20th month from the date in item 3 if box 4(a) above is X'd, or 30th month if box 4(b) is X'd, or else amendments will be considered canceled).**
15. **A declaration of the inventor** (35 U.S.C. 371(c)(4))
- a. ☒ is submitted herewith ☒ Original ☐ Facsimile/Copy
- b. ☐ is not herewith, but will be filed when required by the forthcoming PTO Missing Requirements Notice per Rule 494(c) if box 4(a) is X'd or Rule 495(c) if box 4(b) is X'd.
16. **An International Search Report (ISR):**
- a. Was prepared by ☒ European Patent Office ☐ Japanese Patent Office ☐ Other
- b. ☒ has been transmitted by the international Bureau to PTO.
- c. ☒ copy herewith (1 pg(s).) ☒ plus Annex of family members (1 pg(s).).
17. **International Preliminary Examination Report (IPER):**
- a. ☒ has been transmitted (if this letter is filed after 28 months from date in item 3) in English by the International Bureau with Annexes (if any) in original language.
- b. ☒ copy herewith in English.
- c.1 ☐ IPER Annex(es) in original language ("Annexes" are amendments made to claims/spec/drawings during Examination) including attached amended:
- c.2 ☐ Specification/claim pages # _____ claims # _____
Dwg Sheets # _____
- d. ☐ Translation of Annex(es) to IPER **(required by 30th month due date, or else annexed amendments will be considered canceled).**
18. **Information Disclosure Statement** including:
- a. ☒ Attached Form PTO-1449 listing documents
- b. ☒ Attached copies of documents listed on Form PTO-1449
- c. ☒ A concise explanation of relevance of ISR references is given in the ISR.
19. ☒ **Assignment** document and Cover Sheet for recording are attached. Please mail the recorded assignment document back to the person whose signature, name and address appear at the end of this letter.
20. ☐ Copy of Power to IA agent.
21. ☐ **Drawings** (complete only if 8d or 10a(4) not completed): _____ sheet(s) per set: ☐ 1 set informal;
☐ Formal of size ☐ A4 ☐ 11"
22. ☐ _____ (No.) **Verified Statement(s)** establishing "small entity" status under Rules 9 & 27
23. **Priority** is hereby claimed under 35 U.S.C. 119/365 based on the priority claim and the certified copy, both filed in the International Application during the international stage based on the filing in (country) Great Britain of:
- | | <u>Application No.</u> | <u>Filing Date</u> | | <u>Application No.</u> | <u>Filing Date</u> |
|-----|------------------------|----------------------|-----|------------------------|--------------------|
| (1) | <u>9806788.7</u> | <u>31 MARCH 1998</u> | (2) | _____ | _____ |
| (3) | _____ | _____ | (4) | _____ | _____ |
| (5) | _____ | _____ | (6) | _____ | _____ |
- a. ☒ See Form PCT/IB/304 sent to US/DO with copy of priority documents. If copy has not been received, please proceed promptly to obtain same from the IB.
- b. ☐ Copy of Form PCT/IB/304 attached.

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24. Attached: Notification of the Recording of a Change (2 pages)

25. **Preliminary Amendment:**25.5 Per Item 17.c2, **cancel original** pages #_____, claims #_____, Drawing Sheets #26. **Calculation of the U.S. National Fee (35 U.S.C. 371 (c)(1)) and other fees is as follows:**Based on amended claim(s) per above item(s) ☐ 12, ☐ 14, ☐ 17, ☐ 25, ☐ 25.5 (hilita)

Total Effective Claims	13	minus 20 =	0	x \$18/\$9	=	\$0	966/967
Independent Claims	1	minus 3 =	0	x \$78/\$39	=	\$0	964/965
If any proper (ignore improper) Multiple Dependent claim is present,				add \$260/\$130		+260	968/969

BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(4)): →→ **BASIC FEE REQUIRED, NOW** →→→→A. If country code letters in item 1 are **not** "US", "BR", "BB", "TT", "MX", "IL", "NZ", "IN" or "ZA"

See item 16 re:

1. Search Report was not prepared by EPO or JPO -----	add \$970/\$485		960/961
2. Search Report was prepared by EPO or JPO -----	add \$840/\$420	+840	970/971

SKIP B, C, D AND E UNLESS country code letters in item 1 are "US", "BR", "BB", "TT", "MX", "IL", "NZ", "IN" or "ZA"

(X) → <input type="checkbox"/> B. If USPTO did not issue <u>both</u> International Search Report (ISR) and (if box 4(b) above is X'd) the International Examination Report (IPER), -----	add \$970/\$485	+0	960/961
(only) → <input type="checkbox"/> C. If USPTO issued ISR but not IPER (or box 4(a) above is X'd), -----	add \$690/\$345	+0	958/959
(one) → <input type="checkbox"/> D. If USPTO issued IPER but IPER Sec. V boxes <u>not all</u> 3 YES, -----	add \$670/\$335	+0	956/957
(these) → <input type="checkbox"/> E. If international preliminary examination fee was paid to USPTO and Rules 492(a)(4) and 496(b) <u>satisfied</u> (IPER Sec. V <u>all</u> 3 boxes YES for <u>all</u> claims), -----	add \$96/\$48	+0	962/963

27.	SUBTOTAL =	\$1100	
28.	If Assignment box 19 above is X'd, add Assignment Recording fee of ----\$40	+40	(581)
29.	Attached is a check to cover the -----	TOTAL FEES	\$1140

Our Deposit Account No. 03-3975

Our Order No. 70662

C#

271586

M#

CHARGE STATEMENT: The Commissioner is hereby authorized to charge any fee specifically authorized hereafter, or any missing or insufficient fee(s) filed, or asserted to be filed, or which should have been filed herewith or concerning any paper filed hereafter, and which may be required under Rules 16-18 and 492 (missing or insufficient fee only) now or hereafter relative to this application and the resulting Official document under Rule 20, or credit any overpayment, to our Account/Order Nos. shown above for which purpose a duplicate copy of this sheet is attached.

This CHARGE STATEMENT **does not authorize charge of the issue fee until/unless an issue fee transmittal form is filed**

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NOTE: File in duplicate with 2 postcard receipts (PAT-103) & attachments.

COMPOSITION

This invention relates to compositions containing certain polyurethanes and to their use in ink jet printing.

Ink jet printing methods involve a non-impact printing technique for printing an image onto a substrate using ink droplets ejected through a fine nozzle onto a substrate without bringing the nozzle into contact with the substrate.

There are many demanding performance requirements for colorants and inks used in ink jet printing. For example they desirably provide sharp, non-feathered images having good water-fastness, light-fastness and optical density. The inks are often required to dry quickly when applied to a substrate to prevent smudging, but they should not form a crust over the tip of an ink jet nozzle because this will stop the printer from working. The inks should also be stable to storage over time without decomposing or forming a precipitate which could block the fine nozzle. The most popular ink jet printers are the thermal and piezoelectric ink jet printers.

EP 0769 509 describes a high molecular weight chain extended polyurethane formed from a coloured polyurethane prepolymer for use in ink jet printers with piezo heads. However this composition is not ideal for use in ink jet printers with thermal heads because the use of heat results in nozzle blockage and other operability problems.

There is a need for ink compositions which are suitable for both thermal and piezo ink jet printers, have high colour strength and produce images having a high light-fastness and water-fastness when printed on a substrate.

According to a first aspect of the present invention there is provided a composition comprising a water-dissipatable polyurethane having an Mw less than 25,000, water, colorant, a water-miscible organic solvent and a water-immiscible organic solvent.

The Polyurethane

The water-dissipatable polyurethane has preferably been obtained from the reaction of a mixture comprising the components:

- i) at least one organic polyisocyanate; and
- ii) at least one isocyanate-reactive compound providing dispersing groups.

The water-dissipatable polyurethane has a weight average molecular weight (Mw) less than 25,000 because this can lead to an improved performance of inks containing the polyurethane, especially for use in thermal ink jet printers. The Mw of the polyurethane is preferably less than 20,000, more preferably from 1000 to 15,000,

especially from 1000 to 8000, more especially from 1000 to 7000. Mw may be measured by gel permeation chromatography ("gpc").

The gpc method used for determining Mw preferably comprises applying the polyurethane to a chromatography column packed with cross-linked polystyrene/divinyl benzene, eluting the column with tetrahydrofuran at a temperature of 40°C and assessing the Mw of the polyurethane compared to a number of a polystyrene standards of a known Mw. Suitable cross-linked polystyrene/divinyl benzene chromatography columns are commercially available from Polymer Laboratories.

If the gpc method for determining Mw does not work for any reason then other methods to determine Mw may be used, for example dynamic light scattering.

Component i) may be any organic polyisocyanate known in the art, preferably having two isocyanate groups, and may for example be an aliphatic, cycloaliphatic, aromatic or araliphatic isocyanate. Examples of suitable organic polyisocyanates include ethylene diisocyanate, 1,6-hexamethylene diisocyanate, isophorone diisocyanate, tetramethylxylene diisocyanate, 1,4-phenylene diisocyanate, 2,4-toluene diisocyanate, 2,6-toluene diisocyanate, 4,4'-diphenyl-methane diisocyanate and its hydrogenated derivative, 2,4'-diphenylmethane diisocyanate and its hydrogenated derivative, and 1,5-naphthylene diisocyanate. Mixtures of the polyisocyanates can be used, particularly isomeric mixtures of the toluene diisocyanates or isomeric mixtures of the diphenylmethane diisocyanates (or their hydrogenated derivatives), and also organic polyisocyanates which have been modified by the introduction of urethane, allophanate, urea, biuret, carbodiimide, uretonimine or isocyanurate residues.

Preferred organic polyisocyanates include cycloaliphatic polyisocyanates, especially isophorone diisocyanate, and aliphatic isocyanates, especially 1,6-hexamethylene diisocyanate or hydrogenated 4,4-diphenyl methyl diisocyanate. A small quantity of triisocyanates may be included as part of component i) but this amount preferably does not exceed 5% by weight relative to the total weight of component i). In a preferred embodiment component i) consists of a mixture of diisocyanate and from 0 to 5% (preferably 0%) of triisocyanate by weight relative to the diisocyanate.

Component ii) preferably has at least one, and preferably has two, isocyanate-reactive groups. Preferred isocyanate-reactive groups are selected from -OH, -NH₂, -NH- and -SH. Isocyanate-reactive compounds having three isocyanate-reactive groups may be present, preferably in low levels not exceeding 5% by weight relative to the total weight of component ii). These isocyanate-reactive groups are capable of reacting with an isocyanate (-NCO) group in component i) or component iii).

The dispersing groups provide the facility of self-dispersibility and solubility to the polyurethane in ink media, especially in water. The dispersing groups may be ionic, non-ionic or a mixture of ionic and non-ionic dispersing groups. Preferred ionic

dispersing groups include cationic quaternary ammonium groups, sulphonic acid groups and carboxylic acid groups.

The ionic dispersing groups may be incorporated into the polyurethane in the form of a low molecular weight polyol or polyamine bearing the appropriate ionic dispersing groups. Preferred isocyanate-reactive compounds providing dispersing groups are diols having one or more carboxylic acid groups, more preferably dihydroxy alkanic acids, especially 2,2-dimethylol propionic acid.

The carboxylic and sulphonic acid groups may be subsequently fully or partially neutralised with a base containing a cationic charge to give a salt. If the carboxylic or sulphonic acid groups are used in combination with a non-ionic dispersing group, neutralisation may not be required. The conversion of any free acid groups into the corresponding salt may be effected during the preparation of the polyurethane and/or during the preparation of an ink from the polyurethane.

Preferably the base used to neutralise any acid dispersing groups is ammonia, an amine or an inorganic base. Suitable amines are tertiary amines, for example triethylamine or triethanolamine. Suitable inorganic bases include alkaline hydroxides and carbonates, for example lithium hydroxide, sodium hydroxide, or potassium hydroxide. A quaternary ammonium hydroxide, for example $N^+(CH_3)_4OH^-$, can also be used. Generally a base is used which gives the required counter ion desired for the ink which is prepared from the polyurethane. For example, suitable counter ions include Li^+ , Na^+ , K^+ , NH_4^+ and substituted ammonium salts.

Non-ionic dispersing groups may be in-chain, pendant or terminal groups. Preferably non-ionic dispersing groups are pendant polyoxyalkylene groups, more preferably polyoxyethylene groups. The non-ionic groups may be introduced into the polyurethane in the form of a compound bearing non-ionic dispersing groups and at least two isocyanate-reactive groups or may be introduced as a capping reagents with only one isocyanate-reactive group on a compound bearing non-ionic dispersing groups.

The nature and level of dispersing groups in the polyurethane influences whether a solution, dispersion, emulsion or suspension is formed on dissipation of the polyurethane.

The dispersing group content of the polyurethane may vary within wide limits but is preferably sufficient to make the polyurethane form stable ink-jet printing inks in water and aqueous media. The polyurethane is preferably soluble in water, although minor amount of the polyurethane may be insoluble in water and exist as dissipated particles when mixed with aqueous media or water.

Preferably the proportion of insoluble, water-dissipatable polyurethane is less than 50%, preferably less than 40% and most preferably less than 30% by weight relative to the total weight of the polyurethane. The size of insoluble polyurethane

particulates when dissipated in an ink is preferably less than 100nm, and more preferably less than 60nm.

Preferably the polyurethane is not isocyanate terminated.

Terminating compounds may be used to cap off any excess isocyanate or isocyanate reactive end groups in the polyurethane resulting from the reaction of components i) and ii). Compounds having one isocyanate-reactive group include for example monoalcohols, monoamines and monothiols, especially isopropanol. The terminating compounds may also bear dispersing groups as hereinbefore described. If there are any excess isocyanate-reactive end groups in the polyurethane resulting from the reaction of component ii), these may optionally be capped off by the addition of compounds having one isocyanate group, for example alkyl monoisocyanates.

The polyurethane may be prepared in a conventional manner by reacting the components having isocyanate groups with the components having isocyanate-reactive groups. Substantially anhydrous conditions are preferred. Temperatures of from 30°C and 130°C are preferred and the reaction is continued until the reaction between the isocyanate groups and the isocyanate-reactive groups is substantially complete.

The relative amounts of components i) and ii) are preferably selected such that the mole ratio of isocyanate groups to isocyanate-reactive groups is about 1:1. A two stage process may be utilised where a prepolymer is prepared either in solvent or as a melt, wherein the mole ratio of isocyanate groups to isocyanate-reactive groups is from about 1.3:1 to 2:1, preferably from about 1.4:1 to 2:1, followed by reacting any excess isocyanate end groups with a terminating compound.

Alternatively a prepolymer may be prepared wherein the ratio of isocyanate groups to isocyanate-reactive groups is from about 1:1 to 1:2, preferably from about 1:1 to 1:1.3. The excess isocyanate-reactive end groups may optionally be terminated with a terminating compound.

Preferably the polyurethane is not chain-extended. Preferably the reaction is performed entirely under anhydrous conditions, resulting in no substantial extension of polyurethane on mixing the polyurethane with water or water mixed with chain extenders.

If desired a catalyst may be used to assist polyurethane formation. Suitable catalysts include butyl tin dilaurate, stannous octoate and tertiary amines as known in the art.

The polyurethane of the present invention may be purified if desired in the usual way for colorants used in ink jet printing inks. For example a mixture of the polyurethane and water may be purified by ion-exchange, filtration, reverse osmosis, dialysis, ultra-filtration or a combination thereof. In this way one may remove co-solvents used for the polymerisation, low molecular weight salts, impurities and free monomers.

The Colorant

The colorant is preferably soluble in the polyurethane. Preferably the Colorant is soluble in organic solvents and insoluble in water, for example preferably it is free from sulpho and carboxy groups. In a preferred embodiment the colorant is a dye, more preferably a dye which is soluble in organic solvents and insoluble in water, especially a disperse dye.

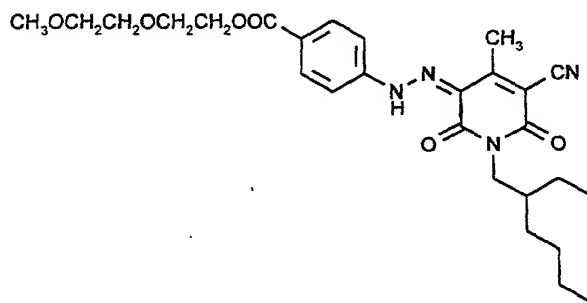
The colorant may be a single component colorant or multi-component colorant, for example it may be a mixture of different dyes. By using a mixture of different dyes as the colorant one may achieve greater flexibility in colour of the ink.

Useful classes of colorants include anthraquinones, phthalocyanines, pyrrolines, triphenodioxazines, methines, benzodifuranones, coumarins, indoanilines, benzenoids, xanthenes, phenazines, solvent soluble sulphur dyes, quinophthalones, pyridones, aminopyrazoles, pyrrolidines, styrylics and azoics. Examples of preferred azoics are monoazo, disazo and trisazo disperse dyes each, of which are optionally metallised and solvent soluble dyes; especially preferred azoics contain heterocyclic groups. The Colour Index International lists suitable disperse and solvent soluble dyes, examples of which include Solvent Blue 63, Disperse Blue 24, Solvent Black 3, Solvent Black 35 and Disperse Red 60.

Further examples of disperse dyes are given in the Colour Index, 3rd Edition, Volume 2, pages 2483 to 2741 and further examples of solvent soluble dyes are given in Volume 3, pages 3566 to 3647 and each of these dyes is included herein by reference

Preferred colorants for use in the inks include:

- $\text{CuPc}(\text{SO}_2\text{NHCH}_2\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_{2.7}(\text{SO}_3\text{H})_{0.3})$ in which Pc is phthalocyanine; and



Water-Miscible Organic solvents

Suitable water-miscible organic solvents include C_{1-5} -alkanols, e.g. methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, tert-butanol and isobutanol; amides, e.g. dimethylformamide and dimethylacetamide; ketones and ketone alcohols, e.g. acetone and diacetone alcohol; C_{2-4} -ether, e.g. tetrahydrofuran and dioxane; alkylene glycols or thioglycols containing a $\text{C}_2\text{-C}_6$ alkylene group, e.g. ethylene glycol, propylene glycol, butylene glycol, pentylene glycol and hexylene glycol; poly(alkylene-

glycol)s and thioglycol)s, e.g. diethylene glycol, thiodiglycol, polyethylene glycol and polypropylene glycol; polyols, e.g. glycerol and 1,2,6-hexanetriol; and lower alkyl glycol and polyglycol ethers, e.g. 2-methoxyethanol, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy) ethanol, 2-(2-butoxyethoxy)ethanol, 3-butoxypropan-1-ol, 2-[2-(2-methoxyethoxy)-ethoxy]ethanol, 2-[2-(2-ethoxyethoxy)ethoxy]-ethanol; cyclic esters and cyclic amides, e.g. optionally substituted pyrrolidones; sulpholane; and mixtures containing two or more of the aforementioned water-miscible organic solvents. Preferred water-miscible organic solvents are C₁₋₆-alkyl mono ethers of C₂₋₆-alkylene glycols and C₁₋₆-alkyl mono ethers of poly(C₂₋₆-alkylene glycols). Cyclic amides are especially preferred.

Water-immiscible Organic Solvents

Suitable water-immiscible organic solvents include aromatic hydrocarbons, e.g. toluene, xylene, naphthalene, tetrahydronaphthalene and methyl naphthalene; chlorinated aromatic hydrocarbons, e.g. chlorobenzene, fluorobenzene, chloronaphthalene and bromonaphthalene; esters, e.g. butyl acetate, ethyl acetate, methyl benzoate, ethyl benzoate, benzyl benzoate, butyl benzoate, phenylethyl acetate, butyl lactate, benzyl lactate, diethyleneglycol dipropionate, dimethyl phthalate, diethyl phthalate, dibutyl phthalate, di (2-ethylhexyl) phthalate; alcohols having six or more carbon atoms, e.g. hexanol, octanol, benzyl alcohol, phenyl ethanol, phenoxy ethanol, phenoxy propanol and phenoxy butanol; ethers having at least 5 carbon atoms, preferably C₅₋₁₄ ethers, e.g. anisole and phenetole; nitrocellulose, cellulose ether, cellulose acetate; low odour petroleum distillates; turpentine; white spirits; naphtha; isopropylbiphenyl; terpene; vegetable oil; mineral oil; essential oil; and natural oil; C₈-C₁₂ substituted pyrrolidones; and mixtures of any two or more thereof Benzyl alcohol is especially preferred.

Preferred Formulations

The compositions according to the first aspect of the invention may be prepared by mixing the polyurethane, colorant, water, water-miscible organic solvent and water-immiscible organic solvent in any order. Suitable mixing techniques are well known in the art, for example agitation, ultrasonication or stirring of the components. The polyurethane may be present in the composition in any form, preferably in a form suitable for inkjet printing, for example the form of a dispersion, emulsification, suspension, solution or a combination thereof.

Preferably the composition is prepared by mixing a dissipation of the polyurethane in a first liquid medium with a solution of the colorant in a second liquid medium, wherein the first liquid medium comprises water and optionally a water-miscible

organic solvent and the second liquid medium comprises a water-immiscible organic solvent and optionally a water-miscible organic solvent.

The weight ratio of water-miscible organic solvent to water-immiscible organic solvent in the ink is preferably 19:1 to 1:1, more preferably 8:1 to 1:1, especially 5:1 to 1:1.

The amount of colorant and water-dissipatable polyurethane contained in the composition will vary according to the depth of shade required. Typically, however, the composition will comprise:

- (a) from 0.5 to 50 parts, more preferably 2 to 20 parts, especially 4 to 12 parts of a water-dissipatable polyurethane (preferably having a weight average molecular weight less than 25,000);
- (b) from 0.1 to 20 parts, more preferably 0.5 to 10 parts, especially 0.5 to 3 parts of colorant;
- (c) from 40 to 90 parts, more preferably from 50 to 80 parts of water;
- (d) from 2 to 30 parts, more preferably 5 to 15 parts, especially from 8 to 12 parts of a water-immiscible organic solvent; and
- (e) from 2 to 60 parts, more preferably from 5 to 25 parts, especially from 10 to 20 parts of a water-miscible organic solvent;

wherein all parts are by weight and the total number of parts of (a) + (b) + (c) + (d) + (e) add up to 100.

The number of parts of the water-dissipatable polyurethane is calculated on a 100% solids basis. For example 50g of a 20% solids polyurethane is taken as 10g of polyurethane.

The composition optionally contains a biocide, for example Proxel GXL (Proxel is a trade mark of Zeneca Limited) or Kathon (Kathon is a trade mark of Rohm and Haas), a fungicide, a rheological agent, e.g. a wax (e.g. beeswax), a clay (e.g. bentonite), an IR absorber, for example Projet 900NP (Projet is a trade mark of Zeneca Limited), or a fluorescent brightener, for example C.I. Fluorescent Brightener 179 and/or UV absorber, for example hydroxy phenylbenzotriazole. Furthermore the compositions optionally contain a surface active agent, wetting agent and/or an emulsifier, for example those described in McCutcheon's Emulsifiers and Detergents 1996 International Edition or in Surfactants Europa 3rd Edition 1996 each of which is incorporated herein by reference.

The composition preferably has a pH from 3 to 11, more preferably from 4 to 10. The pH selected will depend to some extent on the desired cation for any acid groups present in the polyurethane and the materials used to construct the ink jet printer head. The desired a pH may be obtained by the addition of an acid, base or a pH buffer. Where a base is used this is preferably the same base as was used to neutralise the anionic dispersing group during the preparation of the polyurethane.

The viscosity of the composition is preferably less than 20cp, more preferably less than 15cp, especially less than 10cp, at 20°C.

Preferably the composition has been filtered through a filter having a mean pore size below 10 μ m, more preferably below 5 μ m, especially below 2 μ m, more especially below 1 μ m. Such filtration removes particles which could otherwise block the fine nozzles in print heads, thereby improving reliability of the compositions and printers.

The compositions of the present invention have the advantage that they may be used not only in piezoelectric ink jet printers but also in thermal and continuous ink jet printers. Many other inks based on polymers work poorly or even not at all in thermal ink jet printers.

Compositions of the invention form discrete droplets on the substrate with little tendency for diffusing. Consequently sharp images with excellent print quality and little if any bleed between colours printed side by side can be obtained. Furthermore the compositions show good storage stability, wet and light fastness and fastness to both acidic and alkaline highlighter pens.

Preferred compositions according to the invention are used as inks, especially ink jet printing inks. Alternatively the composition may be used as a concentrate which is diluted or otherwise converted into an ink.

A further aspect of the invention provides a process for printing an image on a substrate comprising applying thereto a composition according to the first aspect of the present invention by means of an ink jet printer.

The ink jet printer preferably applies the composition to the substrate in the form of droplets which are ejected through a small nozzle onto the substrate. Preferred ink jet printers are piezoelectric ink jet printers and thermal ink jet printers. In thermal ink jet printers, programmed pulses of heat are applied to the composition in a reservoir by means of a resistor adjacent to the nozzle, thereby causing the ink to be ejected in the form of small droplets directed towards the substrate during relative movement between the substrate and the nozzle. In piezoelectric ink jet printers the oscillation of a small crystal causes ejection of the ink from the nozzle.

The substrate is preferably a paper, plastic, or textile material, more preferably a paper, an overhead projector slide or a textile material, especially paper.

Preferred papers are plain, coated or treated papers which may have an acid, alkaline or neutral character.

According to a further feature of the invention there is provided an ink jet printer cartridge containing a composition as hereinbefore defined.

The invention will now be described by example only. All parts and percentages are by weight unless specified otherwise. In the examples, compounds referred to by reference to CI numbers are the dyestuffs identified by these numbers in the Colour Index International, 3rd Edition, 3rd Revision.

Example 1Stage 1 - Preparation of a Water Dissipatable Polyurethane ("Resin 1")

(completely chain terminated with MPEG750)

Component Number	Component Name	Weight (g)
1	Isophorone diisocyanate	492.21
2	polypropylene glycol of molecular weight 1000	357.8
3	dimethylol propionic acid	150
4	methoxy polyethylene glycol of molecular weight 750	1383.7
5	N-methylpyrrolidone	250
6	dibutyl tin dilaurate	0.8
7	dibutyl tin dilaurate	0.2
8	dimethyl ethanolamine	99.8
9	distilled water	6800

Components 1,2,3 and 5 were charged to a stirred reaction vessel under a nitrogen atmosphere, heated to 50°C and component 6 was added. The reaction exothermed by about 3°C and was then maintained at 90-95°C for 3 hours. A sample of the resultant mixture (3.519g) was removed to determine the %NCO content (found to be 4.71%). Component 4 followed by component 7 were added to the mixture and the temperature was maintained at 90°C until the isocyanate band as determined by an IR spectrum had almost disappeared (2 hours).

Component 8 was added to the stirred mixture at 50°C and allowed to mix for 10 minutes. The resultant mixture at 50°C was dispersed into component 9 at 30°C. During the addition, the temperature of the water rose to about 42°C. The mixture was stirred for a further one hour, cooled to room temperature, and filtered through a 50µm cloth filter.

The resultant water-dissipatable polyurethane in water was found to have a solids content of 24.4% and a pH of 7. The weight average molecular weight (MW) was determined by applying the polyurethane to a gpc column packed with cross-linked polystyrene/divinyl benzene, eluting with tetrahydrofuran at 40°C and assessing the MW compared to a number of polystyrene standards of known MW. The Mw was found to be = 4791 (Mn was 1729).

Stage 2 - Preparation of Ink 1

A sample of a solvent soluble phthalocyanine dye (1g) was dissolved in a mixture of benzyl alcohol (10g) and 2-pyrrolidone (20g) using a sonicator. A mixture of the water-dissipatable polyurethane resulting from Stage 1 (40.9g, 24.4 % w/w dissipation in water) and water (28.1g) were added and the mixture was shaken to give Ink 1 having the formulation:

<u>Component</u>	<u>Amount (g)</u>
Dye	1
Resin 1	40.9 (24.4% solids)
Benzyl alcohol (Immiscible)	10
2-pyrrolidone (Miscible)	20
Water	<u>28.1</u>
	<u>100</u>

Example 2Stage 1 - Preparation of a Water-dissipatable Polyurethane ("Resin 2")

(completely chain terminated with Jeffamine M1000 available from Huntsman Corporation, USA)

Table 1

Component Number	Component Name	Weight(g)
1	Isophorone diisocyanate	492.21
2	polypropylene glycol of molecular weight 1000	357.8
3	dimethylol propionic acid	150
4	Jeffamine M1000	1543.35
5	N-methylpyrrolidone	250
6	dibutyl tin dilaurate	1.0
7	dimethyl ethanol amine	99.72
8	distilled water	7282.5

Components 1,2,3 and 5 were charged to a stirred reaction vessel under a nitrogen atmosphere, heated to 50°C and component 6 was added. The reaction exothermed by about 3°C and was then maintained at 90-95°C for 3 hours. A sample of the resultant mixture (3.519g) was removed to determine the %NCO content (found to be 4.71%). Component 4 was added to the mixture and the temperature maintained at

90°C for a further hour or until the isocyanate band as determined by an the IR spectrum had disappeared.

Component 7 was added to the stirred mixture at 50 °C and allowed to mix for 10 minutes. The resultant mixture at 50 °C was dispersed into component 8 at 30 °C.

5 During the addition, the temperature of the water rose to about 42°C. The mixture was stirred for a further one hour, cooled to room temperature and filtered through a 50µm cloth filter.

10 The resultant mixture of water and water-dissipatable polyurethane was found to have a solids content of 24.2% and a pH of 8.3. The Mw was determined by GPC to be 6597.

Stage 2 - Preparation of Ink 2

15 A sample of the phthalocyanine dye used in Example 1 (1g) was dissolved in a mixture of benzyl alcohol (10g) and 2-pyrrolidone (20g) using a sonicator. A mixture of the water-dissipatable polyurethane described in Example 2, Stage 1 (41.3g 24.19% w/w solution in water) and water (27.7g) were added and the mixture was shaken to give Ink 2 having the formulation:

<u>Component</u>	<u>Amount (g)</u>
Dye	1
Resin 2	41.3 (24.19% solids)
Benzyl alcohol (Immiscible)	10
2-pyrrolidone (Miscible)	20
Water	<u>27.7</u>
	<u>100</u>

Examples 3 to 6

30 The method of Example 2, stage 1 was repeated except that in place of the components indicated Example 1, Table 1, there was used the component indicated in Table 2 below. Components 2a and 2b were used as a mixture in place of the component 2 used in Example 1. All amounts are in grammes. The lower part of Table 2 gives the % solids content, pH, Mn, Mw and surface tension of the resultant Resin.

Table 2

Component Number	Component Name	Example 3	Example 4	Example 5	Example 6
1	IPDI	488.3	483.1	477.9	472.7
2a	PPG	361.7	366.9	372.1	377.3
2b	CHDM	30.0	70	110	150
3	DMPA	120.0	80	40	0
4	JM 1000	1442.8	1493.3	1536.8	1445.5
5	NMP	250	250	250	25
6	DBTL	1	1	1	1
7	DEA	79.8	53.2	26.6	0
8	H ₂ O	7282.5	7282.5	7282.5	7282.5
% Solids		24.4	24.4	24.1	23.9
pH		8.7	8.8	9.1	9.6
Mn		4740	4620	4340	4990
Mw		7500	7190	6680	7530
Surface tension (mN/m)		37.2	36.9	37.7	38.6

PPG = polypropylene glycol of molecular weight 1000

DMPA = dimethylol propionic acid

IPDI = isophorone diisocyanate

CHDM = 1,4-cyclohexane dimethanol

JM 1000 = Jeffamine M1000

NMP = N-methyl pyrrolidone

DBTL = dibutyl tin laurate

DEA = dimethyl ethanolamine

H₂O = distilled water

The water-dissipatable polyurethanes resulting from Examples 3 to 6 were incorporated into inks by the method of Example 1, stage 2, to give inks 3 to 6 respectively.

Comparative Example 1 - High Molecular Weight Polyurethane

Preparation of Ink C1

An ink was prepared using a high molecular weight commercially available polyurethane dispersion called Neorez R961 (Obtained from Zeneca Resins).

A sample of the phthalocyanine dye used in Example 1 (1g) was dissolved in a mixture of benzyl alcohol (10g) and 2-pyrrolidone (20g) using a sonicator. A mixture of

Neorez R961 (26.5g, 34% w/w dispersion in water) and water (32.5g) was added and the mixture was shaken to give Ink C1 having the formulation:

<u>Component</u>	<u>Amount (g)</u>
Dye	1
Neorez R961	26.5 (34% solids)
Benzyl alcohol (Immiscible)	10
2-pyrrolidone (Miscible)	20
Water	<u>32.5</u>
	<u>100</u>

Comparative Example 2 - No Polyurethane

Preparation of Ink C2

A sample of the phthalocyanine dye used in Example 1 (1g) was dissolved in a mixture of benzyl alcohol (10g) and 2-pyrrolidone (20g) using a sonicator. Water (69g) was added and the mixture was shaken to give a Ink C2 having the formulation:

<u>Component</u>	<u>Amount (g)</u>
Dye	1
Benzyl alcohol (Immiscible)	10
2-pyrrolidone (Miscible)	20
Water	<u>69</u>
	<u>100</u>

Ink C2 was found to be unstable to storage because a precipitate formed after standing overnight. Therefore a freshly prepared sample of ink was used for the tests described in Table 1 below.

Example 7 - Ink Jet Printing Using the Inks

Inks 1 to 6 and Inks C1 and C2 were printed onto paper using a Hewlett Packard thermal ink-jet printer. The paper used for Inks 1, 2, C1 and C2 was Conqueror High White Wove plain paper 100g/m² from Arjo Wiggins Ltd and the paper used for Inks 3 to 6 was Xerox acid paper. The properties of the resultant prints are shown in Table 1 below.

The resultant prints using inks according to the invention had very good colour strength and brightness (chroma) as indicated in Table 1 and showed very high water fastness. 0.5ml of water run down a test print only 5 minutes after printing produced virtually no stain on the white paper.

Table 1

Ink	Ink stability	print quality	ROD	wet rub after 5 min
Ink 1	good	good	0.69	9
Ink 2	good	good	0.65	9
Ink 3	stable	good	0.91	10
Ink 4	stable	good	0.91	10
Ink 5	stable	good	0.91	10
Ink 6	stable	good	0.91	10
Ink C1 (Comparative)	poor	did not fire	x	x
Ink C2 (Comparative)	poor	good	0.907	10

ROD is the reflected optical density of the resultant print.

Wet rub after 5 minutes was scored 1 to 10 wherein 1 represents poor rub fastness and 10 represents excellent rub fastness.

X means could not be measured.

Example 8

Further inks may be prepared having the formulations described in Tables 2 and 3 below wherein the following abbreviations are used. These inks may be applied to plain paper using an ink jet printer.

FRU : fructose

PU* : Identifies which of the polyurethanes as prepared in Examples 1 to 6 may be used. The number of parts by weight of PU is shown in brackets.

BZ : Benzyl alcohol

DEG : Diethylene glycol

DMB : Diethyleneglycol monobutyl ether

ACE : Acetone

IPA : Isopropyl alcohol

MEOH : Methanol

2P : 2-Pyrrolidone

MIBK : Methylisobutyl ketone

SUR : Surfinol 465 (a surfactant)

PHO : K_2PO_4

TEN : triethanolamine

NMP : N-methylpyrrolidone

TDG : Thiodiglycol

CAP : Caprolactam

BUT : Butylcellosolve

GLY : Glycerol

- 5 Colorant 1 : $\text{CuPc}(\text{SO}_2\text{NHCH}_2\text{CH}_2\text{CH}_2\text{N}(\text{CH}_2)_3)_{2.7}(\text{SO}_3\text{H})_{0.3}$ wherein Pc is phthalocyanine.
 Colorant 2 : The pyridone dye drawn on page 5 above.

TABLE 2

Colorant	Colorant Content	Water	PU* (parts)	BZ	DEG	ACE	NaOH	(NH ₄) ₂ SO ₄	IPA	MEOH	2P	MIBK	BUT
1	2.0	58	1(10)	4	6						10	10	
2	3.0	61.8	1(10)	5	5		0.2				15		
1	2.1	60.9	2(6)	8							20	1	2
3	1.1	61.9	2(12)	9			0.5				9	5	1
1+2	(3+2)	54	3(5)	15	3	3			6		5	4	
1	5	50	2(15)	20					10				
2	2.4	51.6	1(5)	4		5				6	20	5	1
2	4.1	68.6	3(10)	5	2	10	0.3						
1	3.2	57.8	2(4)	5	4	6			5	4	6	5	
1	5	70	3(10)	6	2	2			1		4		
2	1.8	63.2	2(10)	5							15		5
1	3.3	63.7	2(12)	5		5				2		6	3
2	2.0	62.7	3(5)	10		7	0.3		3		10		
2	5.4	49.6	4(4)	20	2	1					15	3	
1	1.0	63	5(7)	5	4						15	5	

TABLE 3

Colorant	Colorant Content	Water	PU* (parts)	BZ	NMP	SUR	TEN	TDG	FRU	PHO	DMB	CH ₃ NH ₂	CAP
2	1.5	63	1(10)	5		0.15	0.5	20		0.12			4
1	2.5	60	2(15)	6	15							0.2	
1	3.1	64	3(10)	8		0.3		15	0.5	0.2			
2	0.9	63	1(5)	10	20			5					2
2	8.0	40	1(15)	15	15				1		4	0.2	
2	4.0	67	2(10)	10	4				2		6		
1	2.2	67	2(10)	10	3					0.95	5		
2	9.0	54	3(15)	9	7		0.5	10			6		1
2	5.0	57	2(10)	11							7		
1	5.4	54	3(12)	5	17								
1	2.1	65	1(15)	5	5	0.1	0.2	2	0.5	0.1	5		
2	2	56	2(10)	10	5			12			5		
1	8	52	3(20)	5	8						5		2
1	10	63	2(13)	2							12		
1	10	71	1(5)	10			1	1				1	1

CLAIMS

1. A composition comprising water-dissipatable polyurethane having a Mw less than 25,000, water, colorant, a water-miscible organic solvent and a water-immiscible organic solvent.
2. A composition according to claim 1 wherein the polyurethane has been obtained from the reaction of a mixture comprising the components:
 - i) at least one organic polyisocyanate; and
 - ii) at least one isocyanate-reactive compound providing dispersing groups.
3. A composition according to any one of the preceding claims wherein the colorant is soluble in the polyurethane.
4. A composition according to any one of the preceding claims wherein the water-immiscible organic solvent is benzyl alcohol.
5. A composition according to any one of the preceding claims comprising :
 - (a) from 0.5 to 50 parts of a water-dissipatable polyurethane having a Mw less than 25,000
 - (b) from 0.1 to 20 parts of colorant;
 - (c) from 40 to 90 parts of water;
 - (d) from 2 to 30 parts of a water-immiscible organic solvent; and
 - (e) from 2 to 60 parts of a water-miscible organic solvent;wherein all parts are by weight and the total number of parts of (a) + (b) + (c) + (d) + (e) add up to 100.
6. A composition according to any one of the preceding claims wherein the polyurethane has an Mw from 1,000 to 15,000.
7. A composition according to any one of the preceding claims having a viscosity less than 20cp at 20°C.
8. A composition according to any one of the preceding claims which has been filtered through a filter having a mean pore size below 10µm.
9. An ink according to any one of the preceding claims .
10. An ink jet printing ink according to any one of the preceding claims .

11. A process for printing an image on a substrate comprising applying thereto a composition according to any one of the preceding claims by means of an ink jet printer.

12. An ink jet printer cartridge containing a composition according to any one of claims 1 to 10.

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ABSTRACT

A composition comprising water-dissipatable polyurethane, water, colorant, a water-miscible organic solvent and a water-immiscible organic solvent. The compositions are useful as inks for ink jet printers.

RULE 63 (37 C.F.R. 1.63)
DECLARATION AND POWER OF ATTORNEY FOR PATENT APPLICATION IN THE
UNITED STATES PATENT AND TRADEMARK OFFICE

As a below named inventor, I hereby declare that my residence, post office address and citizenship are as stated below next to my name and I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the INVENTION ENTITLED:

Composition based on water-dissipatable polyurethane

the specification of which

is attached hereto
 was filed on _____ as U.S. application serial No.
 X was filed as PCT international application No. PCT/GB99/00655 on 05/03/1999
 and (if applicable) was amended on _____

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above. I acknowledge the duty to disclose all information which is known to me to be material to patentability as defined in 37 C.F.R. 1.56. I hereby claim foreign priority benefits under 35 U.S.C. 119/365 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate filed by me or my assignee disclosing the subject matter claimed in this application and having a filing date (1) before that of the application on which priority is claimed, or (2) if no priority is claimed, before the filing date of this application:

PRIOR FOREIGN APPLICATION(S)

Number	Country	Day/MONTH/Year Filed	Date First Laid	Date Patented	Priority claimed	
			Open or published	or Granted	Yes	No
9806788.7	United Kingdom	31/03/1998				X

I hereby claim the benefit under 35 U.S.C. 120/365 of all United States applications listed below and PCT international applications listed above or below and, if this is a continuation-in-part (CIP) application insofar as the subject matter disclosed and claimed in this application is in addition to that disclosed such in the prior applications. I acknowledge the duty to disclose all information known to

me to be material to patentability as defined in 37 C.F.R. 1.56 which became available between the filing date of each such prior application and the national or PCT international filing date of this application:

<u>PRIOR U.S. OR PCT APPLICATION(S)</u>		<u>Status</u>
<u>Application No. (Serial Code/Serial No.)</u>	<u>Day/MONTH/Year Filed</u>	<u>(patented, pending abandoned)</u>

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

And I hereby appoint Cushman, Darby & Cushman, L.L.P. 1100 New York Avenue, N.W. Ninth Floor, East Tower, Washington, D.C. 20005-3918, telephone number 861-3000 (to whom all communications should be directed), and the below named persons (of the same address) individually and collectively my attorneys to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith and with the resulting patent and I hereby authorize them to act and reply on instructions from and communicate directly with the person/assignee/attorney/firm/organisation who/which first sends/sent this case to them and by who/which I hereby declare that I have consented after full disclosure to be represented unless/until I instruct Cushman, Darby and Cushman in writing to the contrary.

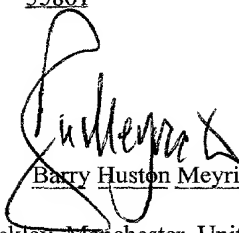
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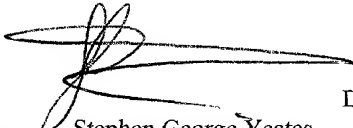
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